CHEMICAL ENGINEERING KINETICS

Third Edition

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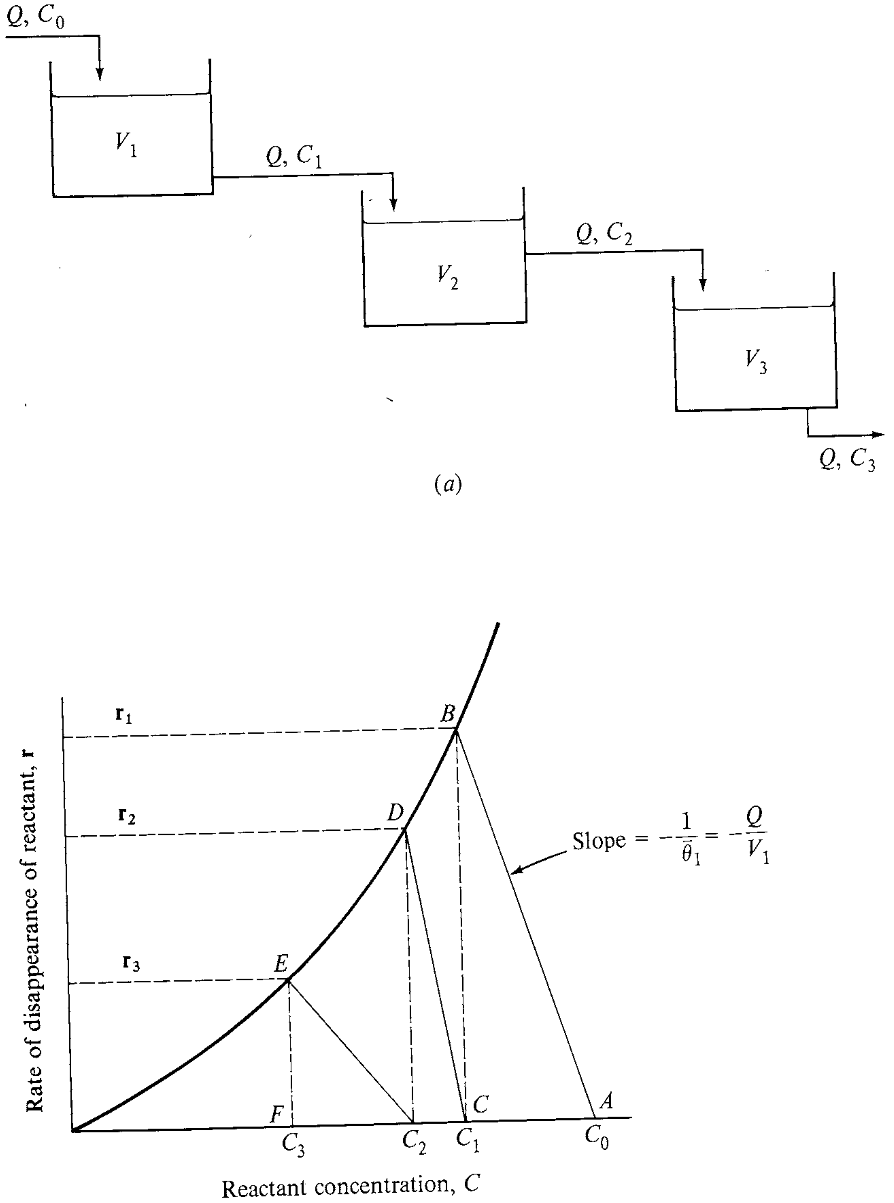
Q, C_0
V_1
Q, C_1
V_2
Q, C_2
V_3
Q, C_3
(a)
r_1
B
r_2
D
Slope = −1/θ_1 = −Q/V_1
r_3
E
F
C
A
C_3
C_2
C_1
C_0
Rate of disappearance of reactant, r
Reactant concentration, C

Figure 4-14 (*a*) Steady operation of three stirred-tank reactors in series. (*b*) Graphical solution for stirred-tank reactors in series.

4-7 Comparison of Stirred-Tank and Tubular-Flow Reactors

The stirred-tank reactor has certain advantages because of the uniform temperature, pressure, and composition attained as a result of mixing. As mentioned, it is possible to operate such a reactor under isothermal conditions even when the heat of reaction is high—an impossibility in the usual tubular type. When a small temperature variation is desired, for example, to minimize side reactions or avoid unfavorable rates, the opportunity for isothermal operation at the optimum temperature is a distinct advantage. Stirred-tank reactors, by virtue of their large

V_3
Q, C_3
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(b) Graphical solution for

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volumes (and hence their large V/F values) provide a long residence time. This, combined with the isothermal nature of the reactor, permits operation at the optimum temperature for a long reaction time. For rate equations of certain types the selectivity in multiple reactions may be greater in tank reactors than in tubular-flow reactors for the same residence time. For other forms of the rate equations the reverse is true. Examples later in this section illustrate this point.

For high-pressure reactions it is usually necessary, because of cost considerations, to use small-diameter tubular reactors rather than tank types. Tank reactors that are to be operated at high pressures require a large wall thickness and complex sealing arrangements for the mixer shaft, factors which increase both initial and maintenance costs. Stirred-tank performance may be achieved in a recycle form of tubular-flow reactor, as illustrated in Fig. 1-7*a*. The diameter may be minimized for high-pressure operation by constructing the reactor in the form of a closed loop of tubing with entrance and exit connections and with a recycle pump in the loop.†

The rate of heat transfer per unit mass of reaction mixture is generally lower in the conventional tank type than in a small-diameter tubular reactor, chiefly because of the lower ratio of surface area (available for heat transfer) to volume in the tank reactors and their lower heat-transfer coefficients. So, in instances where the heat of reaction is high it may be desirable to use a tubular reactor. For example, various thermal reactions of hydrocarbons require significant amounts of thermal energy at an elevated temperature level. This would be difficult to accomplish with a large-diameter reactor because of the limited external heat-transfer surface (per unit mass of reaction mixture) and the low coefficient of heat transfer from the oil in the tank to the tank wall. In the tubular reactors (pipe stills) used in industry the coefficient of heat transfer can be increased by forcing the oil through the tubes at a high speed. It is also apparent that severe difficulties would arise in attempting to provide for efficient stirring under reaction conditions (800 to 1200°F, 300 to 800 lb/in.^{2} abs). The tubular-loop reactor operated at high circulation rates can give complete mixing in a small-diameter tube and high rates of heat transfer. By introducing small solid particles that are free to move, a type is obtained in which there is considerable mixing. Such fluidized-bed reactors also give improved heat-transfer coefficients between the fluid and the wall.

In summary, stirred-tank reactors have been employed on a commercial scale mainly for liquid-phase reaction systems at low or medium pressures. Stirred-tank reactors can be used when the heat of reaction is high, but only if the temperature level obtained in their isothermal operation is satisfactory from other standpoints. If the reactions are endothermic and a high temperature is required, tubular reactors are usually indicated. However, a tank type may be employed as a semibatch unit for a highly exothermic reaction. For example, the production of hexamethylenetetramine by reacting ammonia and formaldehyde (in aqueous solution) is highly exothermic, but the rate of reaction is rapid and 100% conversion is possible over a range of temperature of at least 80 to 100°C. By adjusting the rate of feed and reactor volume, it is possible to add the feed at 20°C and remove enough heat to keep the reaction mixture below 100°C.

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† Practical advantages of loop reactors are discussed in *Process Engineering*, p. 62, December 1973 and *Hydrocarbon Processing*, **55**, 99 (June 1976).

Denbigh and coworkers† have discussed the technical advantages and disadvantages of continuous-stirred-tank reactors, especially in comparison with batch-operated tank reactors. Stead, Page, and Denbigh‡ describe experimental techniques for evaluating rate equations from stirred-tank data. Rase§ presents practical and technical aspects of both plug-flow and stirred-tank reactors.

In stirred-tank equipment the reaction occurs at a rate determined by the composition of the exit stream from the reactor. Since the rate generally decreases with the extent of conversion, the tank reactor operates at the lowest point in the range between the high rate corresponding to the composition in the reactor feed and the low rate corresponding to the exit composition. In the tubular type maximum advantage is taken of the high rates corresponding to low conversions in the first part of the reactor. This means that the tank reactor must have a larger volume for a given feed rate (larger V/F value). Of course, this reasoning does not take into account the effects of side reactions or temperature variations; these may offset this disadvantage of the tank reactor, as illustrated in Example 5-3. Also, the total volume required in a tank-flow reactor can be reduced by using several small units in series. The relation between volumes required in stirred-tank and tubular-flow reactors can be illustrated by reference to a constant volume first-order reaction. Equation (3-5) is applicable for the stirred-tank reactor and gives

$$\frac{V_s}{Q} = \frac{C_0 - C}{\mathbf{r}} = \frac{C_0 - C}{kC}$$

where C refers to the concentration of reactant and $\mathbf{r}$ to its rate of *disappearance*. In terms of conversion of reactants

$$x = \frac{C_0 - C}{C_0} = \frac{k(V_s/Q)}{1 + k(V_s/Q)} \tag{4-17}$$

For the tubular-flow case Eq. (3-18) can be used:

$$\frac{V_p}{Q} = C_0 \int \frac{dx}{\mathbf{r}} = C_0 \int_0^x \frac{dx}{kC_0(1-x)} = \frac{-1}{k} \ln (1 - x)$$

or

$$x = 1 - e^{-k(V_p/Q)} \tag{4-18}$$

Equations (4-17) and (4-18) are plotted in Fig. 4-15 as conversion vs. $k(V/Q)$. For equal flow rates $k(V/Q)$ is proportional to the volume. It is clear that for any conversion the volume required is largest for the tank reactor and that the difference increases with residence time. We can obtain a direct measure of the ratio of

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† K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944), **43**, 648 (1947); K. G. Denbigh, M. Hicks, and F. M. Page, *Trans. Faraday Soc.*, **44**, 479 (1948).

‡ B. Stead, F. M. Page, and K. G. Denbigh, *Disc. Faraday Soc.*, **2**, 263 (1947).

§ H. F. Rase, "Chemical Reactor Design for Process Plants," chap. 6, John Wiley & Sons, New York, 1977.

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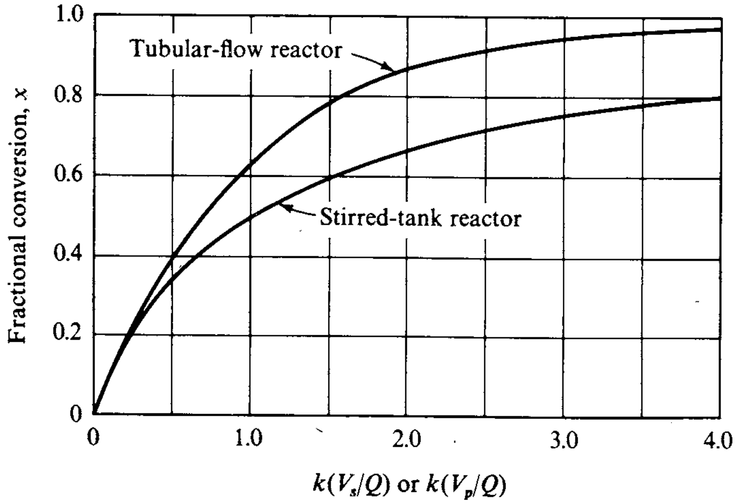

Figure 4-15 Conversion in stirred-tank and plug-flow reactors.

volume V_s of the stirred-tank reactor to volume V_p of the tubular-flow (plug-flow) reactor at the same conversion by equating Eqs. (4-17) and (4-18).

$$\frac{k(V_s/Q)}{1 + k(V_s/Q)} = 1 - e^{-k(V_p/Q)}$$

If α is the ratio of volumes, $\alpha = V_s/V_p$, then the previous equation can be written in terms of V_p and α.

$$\frac{\alpha k(V_p/Q)}{1 + \alpha k(V_p/Q)} = 1 - e^{-k(V_p/Q)} \tag{4-19}$$

If we now replace $k(V_p/Q)$ in Eq. (4-19) with the function of x from Eq. (4-18) and solve for α, we have the ratio of volumes as a function of conversion,

$$\alpha = \frac{x}{(x - 1)\ln(1 - x)} \tag{4-20}$$

This result is plotted in Fig. 4-16 and shows that at low conversions there is little to be gained in using a tubular-flow reactor, but at conversions of 70% or larger more than twice as much volume is required for a stirred-tank unit.†

Selectivity may also be different in stirred-tank and tubular-flow reactors. It has been shown‡ that, depending on the kinetics and nature of the multiple reactions, selectivity obtained in a stirred-tank reactor may be less, the same as, or greater than that for a tubular-flow reactor. Examples of reaction systems for each result are given in Table 4-12. The order of the rate equation is assumed to follow the stoichiometry for each reaction. Since the stirred-tank reactor corresponds to

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† Reactor volume vs. conversion for other forms of rate equations and for different reactor types is given by Wirges and Shah, *Hydrocarbon Processing*, **55**, (April 1976).

‡ T. E. Corrigan, G. A. Lessells, and M. J. Dean, *Ind. Eng. Chem.*, **60**, 62 (1968).

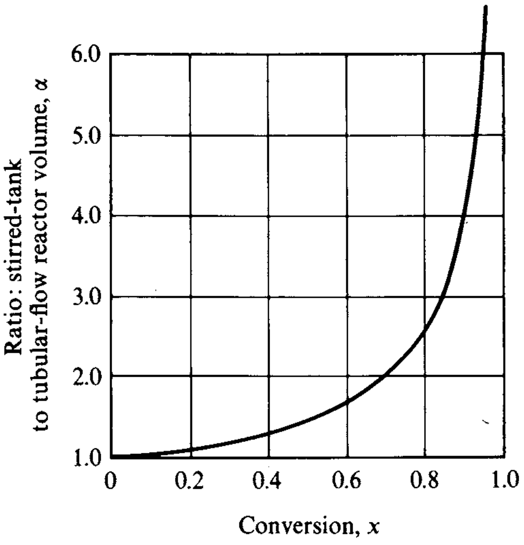

Figure 4-16 Ratio of volumes required for stirred-tank and tubular-flow (plug-flow) reactors.

complete mixing and the tubular-flow unit to no axial mixing, the table shows the effect of mixing upon selectivity. The following example illustrates the method of establishing the conclusions given in Table 4-12.

Example 4-12 Develop equations for the selectivity of product B with respect to D for reaction system 1 of Table 4-12 for stirred-tank and tubular-flow reactors. Assume isothermal conditions and constant density. Let capital letters designate concentrations. In the feed $A = A_0$ and $B = D = 0$.

SOLUTION The reaction sequence is

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_3} D$$

Table 4-12 Effect of mixing on selectivity for various types of reaction systems

Reaction system	Reaction type	Overall selectivity†
1. $A \rightarrow B$ $B \rightarrow D$	Consecutive (first order)	$S_S < S_p$(selectivity of B with respect to D)
2. $A + B \rightarrow R$ $A + R \rightarrow S$	Consecutive (second order)	$S_S < S_p$(selectivity of R with respect to S)
3. $A \rightarrow B$ $A \rightarrow C$	Parallel (equal, first order)	$S_p = S_S$(selectivity of B with respect to C)
4. $A + B \rightarrow C$ $A + B \rightarrow D$	Parallel (equal, second order)	$S_p = S_S$(selectivity of C with respect to D)
5. $A + B \rightarrow C$ $2A \rightarrow D$	Parallel (unequal order with respect to A)	$S_S > S_p$(selectivity of C with respect to D)

† Selectivity, as defined in Chap. 2, is the ratio of the yield of one product to that of another.

In Sec. 2-11 this system was analyzed for a constant-volume batch reactor. Since the tubular-flow reactor will have the same form of mass balance (see Sec. 3-4) as that for the batch reactor the results in Sec. 2-11 can be applied here if t is replaced with the residence time V/Q. Hence the overall selectivity for a *tubular-flow* reactor is given by the ratio of Eqs. (2-89) and (2-90). Since $A/A_0 = 1 - x_t$, this ratio is

$$S_p = \frac{x_B}{x_D} = \frac{[k_1/(k_1 - k_3)][(1 - x_t)^{k_3/k_1} - (1 - x_t)]}{[k_1/(k_1 - k_3)][1 - (1 - x_t)^{k_3/k_1}] - [k_3/(k_1 - k_3)]x_t} \tag{A}$$

For the *stirred-tank* case Eq. (3-5) may be written for components A, B, and D† as follows:

$$\bar{\theta} = \frac{V}{Q} = \frac{A_0 - A}{k_1 A} \qquad \text{or } A = \frac{A_0}{1 + k_1 \bar{\theta}} \tag{B}$$

$$\bar{\theta} = \frac{V}{Q} = \frac{0 - B}{k_3 B - k_1 A} \qquad \text{or } B = \frac{k_1 \bar{\theta} A}{1 + k_3 \bar{\theta}} \tag{C}$$

$$\bar{\theta} = \frac{V}{Q} = \frac{0 - D}{-k_3 B} \qquad \text{or } D = k_3 \bar{\theta} B \tag{D}$$

From Eqs. (B) and (C),

$$\frac{B}{A_0} = x_B = \frac{k_1 \bar{\theta}}{(1 + k_1 \bar{\theta})(1 + k_3 \bar{\theta})} \tag{E}$$

Using this result in Eq. (D) gives

$$\frac{D}{A_0} = x_D = \frac{k_1 \bar{\theta} k_3 \bar{\theta}}{(1 + k_1 \bar{\theta})(1 + k_3 \bar{\theta})} \tag{F}$$

Then the selectivity S_s in the stirred-tank reactor will be

$$S_S = \frac{x_B}{x_D} = \frac{1}{k_3 \bar{\theta}} \tag{G}$$

This result may be expressed in terms of the total conversion of A by noting, from Eq. (B), that

$$k_1 \bar{\theta} = \frac{A_0}{A} - 1 = \frac{x_t}{1 - x_t}$$

Using this result in Eq. (G) to eliminate $\bar{\theta}$ gives

$$S_s = \frac{k_1}{k_3} \frac{1 - x_t}{x_t} \tag{H}$$

Equations (A) and (H) can be employed to calculate S_p and S_s for any conversion. The results are shown in Fig. 4-17 for $k_1/k_3 = 2$. The *relative* position of

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† Alternately, mass balance equations could be written for each reaction and a specific component, and then a total mass balance used to obtain the three required equations (See Examples 4-7, 4-9).

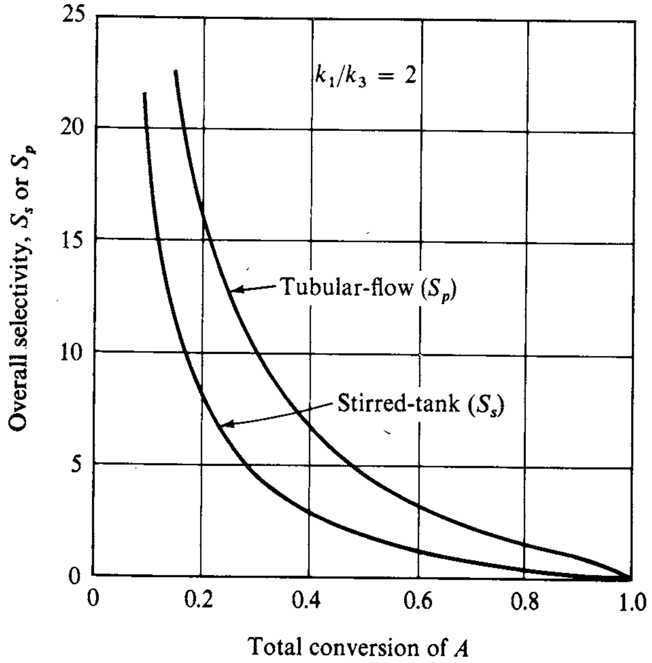

Figure 4-17 Selectivity for consecutive reactions in stirred-tank and tubular-flow reactors.

the two curves would be the same for other values of k_1/k_3. Note that the selectivity of B with respect to D is greater in the tubular-flow reactor for all conversions, although the difference approaches zero as the conversion approaches zero.

Table 4-12 compares selectivities for *single* reactors. For some reaction systems a combination of stirred-tank and tubular-flow units may give higher selectivities than a single reactor of the same total volume. The possible combinations of number and arrangement of reactors and reaction systems are huge. However, the approach to selectivity evaluation is the same and follows the methods described in Example 4-12. A simple illustration of the conversion obtained in a combination of reactors is given in the following example.

Example 4-13 A dilute aqueous solution of acetic anhydride is to be hydrolyzed continuously at 25°C. At this temperature the rate equation for the disappearance of anhydride is

$$\mathbf{r} = 0.158C, \text{ g mol/(cm}^3\text{)(min)}$$

where C is the concentration of anhydride, in gram moles per cubic centimeter. The feed rate to be treated is 500 cm^3/min of solution, with an anhydride concentration of 1.5×10^{-4} g mol/cm^3.

There are two 2.5-liter and one 5-liter reaction vessels available, with excellent agitation devices.

(*a*) Would the conversion be greater if the one 5-liter vessel were used as a steady-flow tank reactor or if the two 2.5-liter vessels were used as reacubular-flow reactors.

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tors in series? In the latter case all the feed would be sent to the first reactor and the product from that would be the feed to the second reactor.

(*b*) Would a higher conversion be obtained if the two 2.5-liter vessels were operated in parallel; that is, if 250 cm^3/min of feed were fed to each reactor and then the effluent streams from each reactor joined to form the final product?

(*c*) Compare the conversions calculated in parts (*a*) and (*b*) with that obtainable in a tubular-flow reactor of 5-liter volume.

(*d*) Would the conversion be increased if a tank-flow reactor of 2.5 liters were followed with a 2.5-liter tubular-flow reactor?

Assume that the density of the solutions is independent of concentrations and that operation is steady state.

Solution Since this is a first-order constant-density reaction, Eqs. (4-17) and (4-18) give the conversions for single-stirred-tank and ideal tubular-flow reactors in terms of residence time V/Q. For multiple-stirred-tank reactors Eq. (A) of Example (4-11) is applicable.

(*a*) For a single 5-liter vessel, $\bar{\theta} = 5000/500 = 10$ min. From Eq. (4-17),

$$x = \frac{0.158(10)}{1 + 0.158(10)} = 0.612$$

For two 2.5-liter reactors in series,

$$\bar{\theta}_1 = \bar{\theta}_2 = \frac{2{,}500}{500} = 5 \text{ min}$$

Substituting in Eq. (A) of Example 4-11 gives

$$x = 1 - \frac{1}{(1 + k\bar{\theta})^2} = 1 - \frac{1}{[1 + 0.158(5)]^2} = 0.688$$

(*b*) For a 2.5-liter reactor with a feed rate of 250 cm^3/min, $\bar{\theta} = 10$ min. Hence the conversion will be the same as for the 5-liter reactor with $Q = 500$ cm^3/min, that is, 0.612.

(*c*) For a single tubular-flow reactor, from Eq. (4-18),

$$x = 1 - e^{-0.158(5000/500)} = 1 - 0.206 = 0.794$$

(*d*) In the first reactor, $\bar{\theta}_1 = 2500/500 = 5$ min. Hence the conversion in the product stream from the first reactor will be

$$x_1 = \frac{k\bar{\theta}_1}{1 + k\bar{\theta}_1} = \frac{0.158(5)}{1 + 0.158(5)} = 0.442$$

When the conversion in the feed stream to a tubular-flow reactor is x_1 rather than zero, integration of Eq. (3-18) gives

$$\theta = C_0 \int_{x_1}^{x_2} \frac{dx}{\mathbf{r}} = C_0 \int \frac{dx}{kC_0(1 - x)} = -\frac{1}{k}[\ln(1 - x_2) - \ln(1 - x_1)]$$

or

$$x_2 = 1 - (1 - x_1)e^{-k\theta}$$

Table 4-13

Type	Conversion, %
Single-stirred tank (5 liters)	61.2
Two stirred tanks in parallel (each 2.5 liters)	61.2
Two stirred tanks in series (each 2.5 liters)	68.8
Stirred tank followed by tubular-flow reactor (each 2.5 liters)	74.6
Single tubular-flow reactor (5 liters)	79.4

The residence time in the second tubular-flow reactor is also 5 min. With a feed of conversion $x_1 = 0.442$, the final conversion would be

$$x_2 = 1 - (1 - 0.442)e^{-0.158(5)} = 1 - 0.254 = 0.746$$

The various results, arranged in order or increasing conversion, are shown in Table 4-13.

In the previous example increasing the number of stirred-tank reactors from one to two (with the same total residence time) caused an increase in conversion from 61.2% to 68.8%. Further increase in number of tank reactors in series would lead to a maximum conversion of 79.4%, the value for a tubular-flow reactor with the same residence time. An infinite number of stirred-tank reactors in series is equivalent to a tubular-flow reactor, provided the total residence time is the same. This may be demonstrated by deriving Eq. (4-18) from Eq. (A) of Example 4-11, which is applicable for equal residence time in each stirred tank. For a total residence time of $\bar{\theta}_t$ Eq. (A) becomes

$$x = 1 - \frac{1}{(1 + k\bar{\theta}_t/n)^n} \tag{4-21}$$

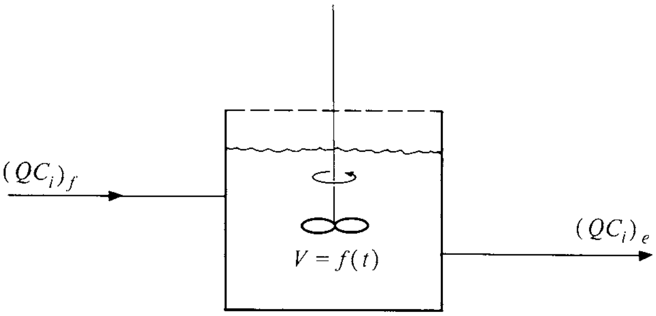

Figure 4-18 Semibatch reactor (stirred-tank type).

It is known that

$$\lim_{n\to\infty}\left(1+\frac{\alpha}{n}\right)^n = e^{\alpha}$$

If we use this result with $\alpha = k\bar{\theta}_t$, Eq. (4-21) becomes

$$x = 1 - e^{-k\bar{\theta}_t}$$

which is the same as Eq. (4-18).

4-8 Non-Steady Flow (Semibatch) Reactors

A tank-type reactor which does not operate at steady-state can be described as a semibatch reactor. Semibatch behavior occurs when a tank-flow reactor is started up, when its operating conditions are changed from one steady state to another, or when it is shut down. Purging processes in which an inert material is added to the reactor can also be classified as semibatch operation.

In addition to applications arising from short-period deviations from steady-state, the semibatch reactor often is used for its own particular characteristics. For example, it is sometimes advantageous to add all of one reactant initially and then add the other reactant continuously. When the heat of reaction is large, the energy evolution can be controlled by regulating the rate of addition of one of the reactants. In this way limited heat-transfer characteristics of tank reactors can be partially eliminated. This form of operation also allows for a degree of control of concentration of the reaction mixture, and hence rate of reaction, that is not possible in batch or continuous-flow reactors. Another example is the case in which the reactants are all added initially to the vessel but one of the products is removed continuously, as in the removal of water by boiling in esterification reactions. The advantage here is an increase in rate, owing to the removal of one of the products of a reversible reaction and to increased concentrations of reactants.

The mass-balance equations for semibatch operation (illustrated in Fig. 4-18) may include all four of the terms in the general balance, Eq. (3-1). The feed and withdrawal streams can cause changes in composition and volume of the mixture in the reactor, in addition to such changes due to the reaction itself. Many operating alternatives exist. One reactant may be present in the initial charge to the reactor and the second reactant added continuously, periodically, or at a continuously varying rate. Similarly, product can be removed in a variety of ways. After presenting general equations, semibatch reactor problems will be illustrated with two special cases (Examples 4-14 and 4-15).

In terms of the molal concentration C_i of species i, volumetric flow rate Q, reactor volume V, Eq. (3-1) takes the form:

$$(QC_i)_f - (QC_i)_e + \mathbf{r}_i V = \frac{d[V(C_i)_e]}{dt} \qquad (4\text{-}22)\dagger$$

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† Note that C_i and $\mathbf{r}_i$ in the reactor are equal to their values in the effluent stream for an ideal stirred tank. Also note that Eq. (4-22) reduces to the usual form for a batch reactor [Eq. (3-2)], if there are no feed or effluent streams, and to Eq. (3-4) for a continuous-flow steady-state reactor.